CHAPTER I

INTRODUCTION

CHAPTER I

INTRODUCTION

1.1 SOLID STATE LUMINESCENCE

The first and oldest record of luminescence is the bioluminescence observed in living organisms which is due to the chemical reaction in the living organism. This was generally observed in fireflies and glow worms. The first written reference of bioluminescence is found in Shih Ching, the "Book of Odes" well before 3000 B.C. Fig.1.1 shows an explanatory comments on bio-luminescence given by the famous Sung Dynasty scholar Zhu Xi which are rather more poetic than discreptive.

However, the first luminescent material was synthesised by Casciarolo of Bologna, Italey in 1603 by heating barium sulphate with charcoal. It emitted feeble blue glow at night after exposure to day light. For this reason it was called 'Lapis Solaris' meaning 'Sun Stone'. This material was immediately investigated thoroughly by Mont Albano (1634), Licetus (1640) and others. The first observation of TL recorded in literature is reported by Robert Boyle to the Royal Society, London in 1663. He observed a strange glimmering light when a diamond is warmed in the dark.

The first definition of luminescence as a non-thermal light emission is found in the book of Licetus, written in 1640, (Refer fig. 1.2).

Until the middle of nineteenth century the phenomenon of light emission by solids after excitation was not subjected to systematic study. The first law in this study was proposed by Stockes (1) in 1852, stating that emitted wavelength is greater than the wavelength of excitation radiation. At about the same time A.H.Becquerel (2) laid the foundations for the experimental investigations of the emission spectrum and duration of after glow by undertaking the systematic study of luminescence. Lenard (3) proposed the kinetics involved in the luminescence of alkaline earth sulphides. The earlier efforts were purely empirical because quantum theory and electron theory were undeveloped.

The term 'luminescence' was first introduced by German Physicist Wiedemann (4) in 1889 as:emission of electromagnetic radiations in excess of thermal radiation. This definition however, is not much accurate. The theoretical explanation for luminescence was given by Randall and Wilkins (5) in 1910 and then by Garlick and Gibson (6). Since then there is a spectacular growth of phosphor studies.

For a long time luminescence was associated with sulphides. Friedrich Hoffmann (7) made much improved calcium sulphide in 1700. Among the activators manganese was one of the known activators. But afterwards number of methods are being devised for their synthesis and new phosphor materials with improved properties are continually being addedto the list. The luminescent materials so synthesised are being used in fluorescent screens for T.V., Cathode ray tubes, electron microscopes, picture display pannels and many other solid state opto-electronic devies.

The rapid development of the luminescence field is not entierely due to the technolggical utility of the phosphors but also because of its importance in basic research. Various theoretical models so far proposed to account the phenomenon are helpful in understanding the electronic processes involved in solids at the atomic levels. Thus from both theoretical and practical point of view luminescence continues to be an active field of scientific research.

1.2 DEFINITIONS

1.2.1 Luminescence

In general, luminescence is a phenomenon in which the material absorbs energy and reemitts the energy as visible or near visible radiation. The emitted radiation is non thermal in origin (8) and it must be distinguished from Raman, Compton, Rayleigh scattering and Cherenkov radiation. The time delay in luminescence emission after excitation is longer than 10^{-9} seconds, where as in later it is of the order of 10^{-14} seconds (9).

According to the mode of excitation, the luminescence phenomenon is classified as follows :

a) Photoluminescence : produced by absorbtion of ultraviolet or visible radiations.

b) Radioluminescence : caused by bombardment with high energy particles or radiations such as x-ray,gamma rays etc.

c) Cathodoluminescence : a special case of radioluminescence, produced by cathode rays.

d) Electroluminescence : caused by application of electric field.

e) Sonoluminescence : produced by sound waves usually of ultrasonic variety.

f) Triboluminescence : produced by utilization of mechanical energy.

g) Chemiluminescence : Occures as a product of chemical reaction.

h) Bioluminescence : a chemiluminescence in living organism.

i) Galvanoluminescance : produced during electrolysis in galvonic cell.

j) Thermoluminescance : Thermoluminescence, however, does not refer to the thermal excitation but rather to the thermal stimulation of luminescent emission when the sample is excited by other means.

Many times the combination of above types are used and are as follows :

a) Photo-electroluminescence : refers to radiation modulated electroluminescence.

b) Electro-photoluminescence : refers to enhancement of light intensity by applied field.

c) Electro-thermoluminescence : refers to thermoluminescence enhanced by the applied field.

d) Photo-transferred thermoluminescence : refers to thermoluminescence stimulated by radiation dose at high temperature, usually beyond 400°c.

1.2.2 Fluorescence and phosphorescence :(fig.1.4)

The general term of luminescence is classified either as fluorescence or phosphorescence depending on the duration of emission after the removal of exciation. Garlick (6) defines fluorescence as emission of light during excitation and phosphorescence, after excitation is removed.

According to Leverenz (10) and Kroger (11) a luminescence emission which lasts up to the inital 10^{-8} seconds after exciattion is fluorescence, while the subsequent is to be referred as phorsphorescence.

1.3 Phosphors and their classification

Phosphor is a term applied in industrial technology to a luminescent material, particularly one ~~artificially~~ artificially produced for use in various appldcations such as TV tubes, radar screens, fluorescent lamps etc. They may be either organic or inorganic in nature but inorganic phosphors are commercially important (18).

Conventional phosphors consists of one and some times more of the following components :

i) the host

ii) one or more activators (acceptors)

iii) a co-activator or a charge compensator (donor).

Phosphors are classified as (a) phosphor in pure form and b) impurity activated phosphors.

1.3.1 Phosphors in pure form

Certain phosphors show luminescence when they are in the pure form. They are known as self activated phosphors, eg. ZnO, many tungstates, molybdates and diamond (6, 13).

1.3.2 Impurity activated phosphors

Impurity activated phosphors show better luminescence than the pure one. For activation small amount of foreign ions are added in to the base compound called a~~s~~ host lattice or matrix material. The impurity which causes luminescence is called activator. The second impurity introduced in addition to first, to enhance the luminescence is called as co-activator. It is observed that due to presence of some impurities (eg. Fe, CO, Ni etc.), the luminescence intensity decreases. Such impurities are called as killers or poisons.

1.4 Localised energy levels in forbidden gap :

The impurities or lattice defects give rise to discrete energy levels in the forbidden energy gap of an insulator or semiconductor. These localised discrete energy levels are classified as

A) Luminescence Centre

These are the energy levels responsible for the spectrum of emitted luminescence. The absorption and emission properties of these centres are the characteristics of activator ions and the base material. These centers possess high capture cross-section for excited electrons and much greater probability for radiative transition than for non-radiative transition (14).

B) Killer Center

These are discrete localised energy levels which possess a small capture cross-section for excited electron and much greater probability for non-radiative transition than for the radiative transition.

C) Electron traps

A localised level which can capture an excited electron, produced in the centers or else where in the crystal, without allowing an electron to fall directly in to a normally filled level is called an electron trap or just a trap.

D) Hole Trap

These are localised levels just above valence band capable of capturing a positive hole.

E) Meta-stable state

These are energy states existing within the forbidden region, which can be excited by electron bombardment but not by photo excitation. A transition from metastable level to normal state is forbidden. The transition from higher level to metastable state is permitted. Representative life times of meta-stable levels are of the order of 10^{-2} to 10^{-4} seconds.

1.5 Mechanism of Photoluminescence

The mechanism of photo luminescence involves four processes, (i) Excitation, (ii) emission, (iii) transfer of energy during excitation and emission and (iv) storage of the part of absorbed energy during excitation.

1.5.1 Excitation and Emission

Several schemes have been proposed to explain these processes. Some of them are as follows :

i) Classical Configuration Coordinate Curve Model :

The configuration coordinate curve model is represented in fig. 1.5. It was introduced by Van-Hippel (15) and was applied by Seitz (16) to explain the luminescence behaviour. In figure the ordinate represent the total energy of the system for the ground and excited states of the center, while the abscissa the 'configuration coordinate' which specifies the configuration of the ions around the center. The equilibrium position of the center in the ground state is represented by the point A. If the centerabsorbs light energy, it is raised to the excited state at B. The transition is vertical in accordance with the Frank Condon principle. From B the center relaxes to new equilibrium state C, the state corresponding to the minimum energy of excited state. The energy difference between B and C is given off as lattice vibration. Having reached the centre at this new equilibrium position it returns to the ground state 'D' by giving luminescence emission. The center finally relaxes from D to A again giving up energy to the lattice vibration. Thus the emitted energy is smaller than the absorbed one and explains the stoke's shift.

ii) Energy band model :

The energy band model (17, 18) is illustrated in fig.1.6. According to this model, the phosphors which are usually semiconductors or insulators are described in terms of valence band (F) and and conduction band (C) with localised energy level in the forbidden region. The localised energy level are associated with impurities or imperfections in the host lattice. In fig. (1.6) such levels are shown. The level 'L' represents ground state of the luminescence center, while levels T_1 and T_2 represent electron and hole traps respectively.

The act of excitation and emission takes place as follow : Absorption of light energy in the phosphor excites luminescence center from ground state (L) to the excited state (S) by raising the electron into conduction band. Such excited center then captures an electron from the conduction band and returns to its ground state by giving luminescence emission.

If the absorbed energy in the phosphor is equal to the separation between the valence and conduction band it also excites electrons (E) from valence band into conduction band creating holes (H) in the valence band. This absorption is known as the fundamental absorption band. However, such electron and hole pairs normally do not recombine radiatively, (19,20).

iii) Schon-Klasen's Model :

This model was proposed by Schon (21) and elaborated by Klasen and his co-workers (22,23,24). Fig. 1.7 illustrate the model for the case of single luminescence centre. The ground level 'L' of the luminescence center is assumed close to the valence band. On absorption of light in the fundamental absorption band, a free electron and a hole are created. The electron moves to the conduction band while the hole diffuses through the valence band and captures an electron from the luminescent centre. This excites the luminescent center. The free electron after migrating in the conduction band falls into the empty center which give emission of light.

iv) Lambe-Klick's Model :

In this model (25) the ground state of the luminescent center ◊ L) is assumed close to the conduction band fig. 1.8. With absorption of light photon, a free hole and electrons are produced. The hole diffuses to the center where it captures the electron from the center. This transition gives rise to luminescence. Subsequently the electrons from conduction band diffuses to the center and gets captured there thus completing the cycle.

v) Williams and Prener's Model :

In the model proposed by William (26) and Prener (27), two centers are involved (fig. 1.9).

The ground level (I) of the first center is assumed close to the valence band while the excited level (II) of second is assumed close to the conduction band. After absorption of the energy in the fundamental absorption band a free hole and an electron are produced. The excited level (II) captures qn electron from the conduction band while the holes in the valence band capturesan electron from the ground level (I) and thus leaves it empty, the emission then takes place by the transition from level II to the I.

1.5.2 Energy Transfer

In phosphor systems where absorption and emission of light energy take place at same center no energy transfer is involved.

However, in system in which absorption and emission are not confined to the same center, energy is transferred from absorption center to the emission one. It occurs in two ways, (A)Energy transfer with no movement of charge carriers and (B)Transport of energy by charge carrier.

A)Energy Transfer with no movement of charge carriers :

There are three mechanisms for transfer of energy in such cases.

i) Cascade Mechanism

In this type of mechanism (28) one center on absorbing excitation energy emits radiation (Primary emission). This emitted radiation is then absorbed by second center which finally emits luminescence (secondary emission). This mechanism is most effective in those cases where the primary emission overlaps the absorption spectrum at the secondary emission system.

ii) Resonance Transfer

Here the transfer of energy from absorbing system to the emitting system is accomplished by a quantum mechanical ~~[illegible]~~ resonance process (29,30), such as electric dipole field overlap, electric dipole-quadrupole field overlap or by exchange interaction. The efficiency of processes depends upon the distance over which the energy is transferred.

iii) Excitation Migration

The non-conducting excited electron-hole pairs are known as excitons. Because of their interaction with phonons they do not remain localised but migrate through out the crystal transferring the energy. In such process the excitons transfer excitation energy from one point to another by moving quickly through the lattice without contributing to the electrical conductivity (31).

B) Energy Transfer with movement of charge carrier

In this mechanism energy is transferred by electron and hole migration. The process is same as that involved in Schon-Klasen's and Lambe-Klick's model during excitation and emission.

1.5.3 Energy Storage

After the removal of excitation source, many phosphors store part of absorbed energy during excitation. This is due to the trapping of the excited electrons, in trap levels. The energy required to liberate a trapped electron is known as the 'activation energy' and is always denoted by E. The energy E is also known as the 'trap depth' as it is the energy difference between the traping level and corresponding excited level.

A) Phosphorescence Decay

Phosphorescence decay is diminishing after glow under isothermal conditions, observed from 10^{-8} seconds after removal excitation. It arises due to the release of trapped electrons in trapping levels during excitation.

The mechanism of phosphorescence decay can be followed from the energy band model of Fig. (1.6). An electron raised into the conduction band by absorbing light energy may according to minimum energy principle fall into a trap (T_1) instead of immediately recombining with a center. After some time the trapped electron returns to ground state via a conduction band giving rise to phosphoresence. Process (H E T S L).

B) <u>Thermoluminescence</u> :

If a previously excited and sufficiently decayed phosphor is heated at constant rate then light is emitted. This phenomenon is known as thermoluminescence. In thermoluminescence, heat is not the excitation agent but it only acts as stimulant. Hence it is also called as thermally stimulated luminescence (TSL). The excitation may be achieved by any conventional agent like uv rays, ionising radiations, mechanical vibrations and so on. Phosphorescence at any temperature after the removal of [illegible] exciatation is nothing but isothermal decay of TL at that temperature.

In thermoluminescnece, the electrons trapped during exciatation are released by thermal activation. Such released electrons get combined with luminescent centers via conduction band and give the TL emission.

The variation of total light output versus temperature is known as "Glow curve". The temperature at which TL output is maximum is called as peak temperature and it is a measure of trap depth. The peak temperature and peak intensity are the functions of position of trapping level below the conduction band and the number of electrons trapped in that level. The peak intensity is also a function of heating rate. This is because, at higher heating rates, the rate of release of electrons from the traps increases and hence TL intensity also increases. The TL glow curve may exhibit many peaks depending on the nature of the material These peaks will corresponds to traps of different depths.

1.6 Mechanism of electroluminescence

Substances which emit electromagnetic radiation (visible or near visible) due to the application of an electric field (AC or DC) are called electroluminescent materials and the phenomenon involved in the emission of light is termed as electroluminescence (EL). The mechanism of electroluminescence consists of three stages (i) excitation, (ii) transfer of energy from the site of excitation to the site of emission, and (iii) recombination (32).

1.6.1 Excitation :

The exciatation of EL takes place by a supply of energy (potential or kinetic or both) to the charge carriers (generally electrons). The different excitation mechanisms proposed are,

i) Field ionisation of valence electrons and impurities:

The possibility of exciting an insulator with an intense electric field in such a way as to excite valence electrons in to the conduction band was first pointed out by Zener (33). The transfer of valence electron may take place by quantum mechanical tunneling process (34) producing a free electron and free hole simultaneously. As the breakdown field competes with both of these processes, a activator systems having a low ionization energy in dielectric phosphors (large band gaps) should be more conductive to EL by this process (Piper et al. 1955).

ii) Injection EL

Injection of minority carriers may occure either at an electrode contact or a P-N junction. In a surface contact, the interface may possess ohmic characteristics or is capable of rectification and, thus, its behaviour is governed by factors like the difference in work functions, the position of fermi level in the semiconductor, nature of the intermediate chemical or physical barrier layer, surface states and the concentration of the donor and the acceptors. The barrier formed in the rectifying contact is known as Mott Schottky barrier. In this type of barrier minority carriers can be injected into the interior of the semiconductor. Injection EL occures in following structures.

a) P-N junection :As shown in the fig.(1.10) the potential energy of electrons in the N region is raised under a forward bais, which allows the flow of electrons in to the P region and similarly the flow of holes in to the N region. As soon as an overlap of electrons and holes occures, they recombine radiactively. The arrow represents a band to band recombination. The light emitting diodes (LED's) often have one side of the junction more heavily doped than the other. Due to this, the carriers in the larger doped side have the benifit of the reduction in the barrier height.

b) Heterojunctions : As shown in fig. (1.11) the large bandgap materials acts as a source of injected charge carriers and that with small band gap as luminescent region.

c) Schottky barriers : Fig.(1.12) shows the inversion layer in an N type material. Under a forward bias, the bands are flattened allowing the injection of minority carriers into the bulk matrix where they recombine radiatively.

d) Metal-Insulator-Semiconductor (MIS) structure :

In this structure the band bending can be controlled by an applied voltage and an inversion layer can be introduced by one polarity. The carriers so accumulated at the surface can be injected by reversing the polarity of metal electrode. This is shown in fig. (1.13). The holes accumulated at the surface are injected and recombination takes place. (shown by arrow). If the insulator is made thin the injection of electrons can take place by tunneling.

iii) Radiative tunnelling : As shown in fig. (1.14) electrons from the conduction band tunnels into the gap where it makes a radiative transitions to the valance band or an empty state in the band gap. For this process to occur, the semiconductor should be degenerately doped on both sides.

iv) Acceleration -Collison EL :

A process, found in most materials like ZnS is based on the acceleration of the electrons in the conduction band followed by a collison excitation of the luminescence centers. Its various stages are shown in fig. (1.15). A Mott Schottky exhaution barrier is suggested to account for the stability against breakdown at the field strength at which EL excitation takes place. (Piper et al, 1958). The field in the barrier and the thickeness of the barrier increases as the square root of the voltage. The source of charge carriers may be deep donors, acceptors or traps which are field ionised.

v) Breakdown luminescence :

By gaining sufficient energy from the electric field, electrons and holes are multiplied and thereby form an avalanche breakdown.

The pairs created in this way, recombine radiatively.

1.6.2 Energy transfer

The mode of energy transfer from the point of excitation to the site of emission occures via movement of charge carriers. The flow of energy due to the transport of charge carriers depends on the concentration gradient, the electric field intensity and the concentration of the trapping states.

The transport of energy from the electrically excited system to the emitting system can also occur by mechanisms not involving electronic charge carriers i.e by

i) Cascade transfer mechanism,
ii) Resonance transfer mechanism
iii) Exciton migration mechanism.

1.6.3 Recombination

In the process of recombination various transitions takes place from upper energy state to empty lower energy states. The transitions can be radiative or non radiative.

i) Band to band transitions :

In direct semiconductorsit occures between conduction and valence bands and in the case of indirect semiconductor it requires emission or absorption of a phonon to complete the lowest energy transition across the energy gap.

ii) Transition between band and impurity :

A radiative transition can occure between an impurity state and intrinsic band and its probability is high, if the impurity state is deep.

iii) Transitions of a localised centre :

In large bandgap materials impurities can be excited without ionising them, i.e. without exciting their electrons to the conduction band.

iv) Transitions at isoelectronic centres :

Such centres are formed by replacing an atom of the host crystal by another but with the same valency. Radiative transition can occure in the excitation bound to an isoelectronic centre.

v) Donor acceptor transitions :

Efficient transitions can also occure **between** donor and acceptor levels and such transitions are found in LEDs and in phosphors.

Transitions from upper to lower energy states occurring without emission of photons are termed as - non radiative transitions and can occure through a number of processes such as i) Multiphonon emission at the intersection of the ground and excited state configuration diagram. The electron can escape the excited state and return to its equilibrium position by generation of several phonons.

ii) Auger effect, where in a recombining electron can transfer the energy to another electron in the excited state. This second electron goes to a still higher energy state and returns to lower energy state by multiphonon emission

iii) Non radiative defects such as surface recombination crystal defects providing regions, where a localized continuum of states can bridge the energy gap and claster of vacancies of impurities can form non radiative centers.

Some important requirements of a good EL phosphor are :

i) its electron traps should be shallow

ii) its activation energy for the escape of holes from the ionised activator levels should be as large as possible &

iii) should have a cubic structure which is more favourable for EL emission.

1.7 Kinetics of luminescence

The kinetics of luminescence is concerned with the mechanism involved in the recombination of electrons with luminescence centres. There are three modes of kinetics involved in a luminescence process, viz.

i) monomolecular kinetics (First order Kinetics)

ii) Bimolecular kinetics (second order Kinetics)

iii) Intermediate Kinetics (General order Kinetics)

i) Monomolecular Kinetics :

If traps are situated close to luminescence centers and if a very small movement of electron is needed to recombine with luminescence center then the kinetics of luminescence process is said to be monomolecular (8). In the monomolecular kinetics the probability of retrapping is negligible i.e. process of recombination is dominant (31, 35).

ii) Bimolecular Kinetics :

In this case the traps are located away from the luminescence centers and the electrons have to go large displacement for recombination with luminescence centres, then the kinetics of luminescence process is said to be bimolecular or second order. In bimolecular kinetics process of retrapping is dominant (31, 35).

iii) Intermediate Kinetics

When the order of kinetics is neither uniquely monomolecular nor uniquely bimolecular then it is called as intermediate kinetics or general order kinetics. In this case the traps are supposed to be distributed in the vicinity of luminescence centers in such a way that the probability of retrapping of electrons in deeper traps is small but not negligible. The occurrance of such an intermediate order of kinetics is shown to be feasible by several workers (36, 37).

1.8 Brief Survey of luminescent materials

The phenomenon of luminescence is observed in number of naturally existing materials, however, impurity activated luminescent materials have better luminescence output and efficiency. The various luminescent materials which are thoroughly investigated and now used in number of applications are alkali halides, sulphates, borates, sulphides, ~~carbond~~ carbonates etc. Extensive work on alkali halides ultimately led to the wellknown phosphor LiF:Mg,Ti used in radiation dosimetry. This phosphor is being manufactured by Harshaw chemical Company under trade names TLD-100, TLD-600 & TLD-700 (38). Study of LiF crystal doped with various activators has been carried out by Kathuria (39).

$CaSO_4$ phosphors doped with rareearths have been studied by Nambi K.S.V. (~~2~~ 40) and found that these phosphors have better sensitivity than LiF or CaF_2 phosphors. He has also found that impurities having ionic radii close to radius of Ca^{2+} ion (Dy^{3+}, Tm^{3+}) have maximum TL output, while La^{3+}, Yb^{3+}, & Lu^{3+} whose ionic radii are largely different from that of Ca^{2+} do not yield any significant increase in TL output. $CaSO_4:T_m{}^{3+}$ can be used as radiation detector, for measurement of environmental radiation in BARC.

Calcium sulphide is one of the oldest known fluorescent materials having a fine violet luminescence and very long after glow. Lehmann has carried out an extensive experimented investigation on this class of phosphor with 31 different elements as possible activators. Number of other workers have studied the sulphide phosphors doped with various activators (41, 42, 43, 44, 45, 46, 47).

Among the various activators Mn is proved to be a good activator in different phosphors. Mn can be used as a universal dopant in nearly all inorganic phosphors (38). Mn is almost exclusively responsible for the TL emission spectra of all types of natrual calcites. It is also one of the most efficient dopant for TL emission in CaF_2 and $CaSO_4$. Photoluminescence studies of Mn doped sulphates show that it is not an efficient emitter of luminescence unless a co dopant like Ce^{3+} is stimulataneously used to sensitise it. It has been explained that Mn^{2+} ion receives the excitation energy from the codopant impurity ion (48). The stu ~~have been~~ of Mn along with rare earth in $CaSO_4$ phosphors have bee studied (38). Rare earths are also found to be efficient activators in borates (49).

1.9 Statement of Problem :

To understand the role of Mn in CaS and various effects on doping of rare earths in presence of Mn or independently, efforts are done in this dissertation. Since Mn is almost proved to be good activator in materials (phosphors) like sulphates, it would be worth understanding effect of Mn as an activator or otherwise in CaS. Since luminescence out put of Mn doped phosphor is found to increase in presence of other activators like Ce, it is found proper to study this aspect in presence of rare-earths. Since sulphides of composition CaS:Mn:RE are not extensively studied, planning is channelised to prepare phosphors of this composition and to find out suitable rare-earth amongst chosen which are found proper for other hosts, Optimum concentration of both Mn and Rare-earth (RE) in CaS and to gain the information about trap depth, mechanism of luminiscence, kinetics involved in luminescence process and distribution of traps.

1.9.1 Phosphorescence decay

In the present investigation attempt has been made to plot Decay Curves and to find out nature of decay curve, nature of decay law, types of kinetics, distribution and population of traps at room temperature.

1.9.2 Thermoluminescence

An attempt has been made to investigate the effect of addition of impurities (Mn, Sm) on glow curves. Using glow curves, the activation energy, the frequency factor and order of kinetics of luminescence process have been estimated.

1.9.3 Electroluminescence

A.C.electroluminescence measurements have been carried out to investigate the possible relationship between brightness-voltag and brightness-frequency. Effect of concentration of activators have been studied.

1.9.4 Thermally Stimulated Conductivity

An attempt is made to study the variation of conductivity with temperature

REFERENCES

1. Stokes, G.G. 'On the Refrangibility of light" Phil.Trans, Roy. Soc. London A 142, II 463 (1852).

2. Becquerel, E., "La Lumiere, ses causes et ses Effects", Gauthier-Villars Paris, (1867).

3. Lenard, P., Schmidt, F., and Tomoschek, R.,Handbuch der Expt. Phys.,23 parts-I and II, Akad.Verlagsges, Leipzing(1928

4. Wiedmann, E., Wied·Ann. 37, 177 (1889).

5. Randall, J.J. and Wilkins, M.H.F. Proc., Roy Soc., A 184, 366 (1945).

6. Garlick, G.F.J. and Gibson, A.F., Proc. Roy. Soc. 60, 574, (1948).

7. Hoffmann, H., Chymia rationalis et experimentalis, Berlin, (1784).

8. Curie, D., Luminescence in crystalls, (Method and Col. Ltd., London, 1963).

9. Williams F.E. 'Luminescence of Inorganic Solids', edited by P. Goldberg, New York, P.2 (1966).

10 Leverenz, H.W., Science (London), 109, 183, (1943).

11 Kroger, F.A., Physica 14, 425 (1948).

12 "The Harper Encylopedia of Science", Edited by James R. Newman, Vol. III. M.through R.P-910.

13 "Symposia on Diamond," Proc., Indian Acad. Sci.A 19, 189(1944).

14 Bube R.H. Phy. Rev.80, 655 (1950)

15 Von-Hippel A.Z.Physik, 101, 680 (1936)

16 Seitz, F. Trans. Farady Soc. 35, 79 (1939)

17 Bloch F. 2, Physik 52, 555 (1928).

18 Johnson, R.P., J. Opt. Soc. Amer 29, 387 (1939).

19 Abhyankar, M.D., Ph.D.Thesis, Univ. of Sagar, (1968)

20 Lawangar,R.D., Ph.D. Thesis, S.U. (1974).

21 Schon, M. Z. Physik 119, 463 (1942)

22 Klasens, H.A., Nature 158, 306 (1946)

23 Klasens H.A., Ramsden W. and Quantie, C.J. Opt. Soc. Amer, 38, 60, (1948).

24 Wise, M.E. & Klasens, H.A. J. Opt. Soc. Amer, 38, 226 (1948).

25 Lambe, J. and Klick C.C., Phys. Rev. 98, 909 (1955).

26 Williams, E.E., T.Phys. Chem.Soc. Solids, 12, 265 (1960).

27 Prener, J.S. & Williams F.C., J. Phys. Rad, 17, 667, (1956).

28 Klick, C.C. and Schulman, J.H. Solid State Phys. Vol. 5, Academic Press, New York, (1957).

29 Shulman, J.H., Ginthner, R.J. and Klick C.C., J.Electrochem. Soc. 97, 123 (1950).

30 Dexter, D.L., J. Chem., 21, 836 (1953).

31 Halperin, A. and Braner, A.A., Phys. Rev. 117, 408 (1960).

32 Shashi Bhushan, Nucl.Tracks, Vol. 10, NO. 1/2,pp. 215-224, (1985).

33 Zener, C.M., Proc. Roy Soc. (London) 145 A, 523 (1934),

34 Leverenz, HW. "An Introduction to Luminescence of Solids", (Dover Publications Inc., New York, 1968).

35 Riehl, N. and Schon, M. Z.Physik, 114, 682 (1939)

36Chen, R. J. Electrochem. Soc. 116, 1254 (1989).

37 Kathuria, S.P. and Sunta,C.M., J. Phys. D: Appl. Phys., 12, 1 (1979).

38 Bapat, V.N., Ph.D. Thesis, Bombay University, 1977.

39 Kathuria, el.al., "Gamma rays Induced Thermoluminescence, and Phototransferred thermoluminescence in Lithium fluoride". B.A.R.C. (1979).

40 Nambi K.S.V, Ph.D.Thesis, Gujarat Univ. 1974

41 Patil M.G., Ph.D. Thesis, Shivaji University, Kolhapur, 1981.

42 Lawangar, R.D., Ph.D.Thesis, Shivaji University, Kolhapur, 1974.

43 Shalgaonkar C.S., Ph.D.Thesis, Shivaji University, Kolhapur, 1975.

44 Pawar S.H., Ph.D.Thesis, Shivaji University, Kolhapur, 1974.

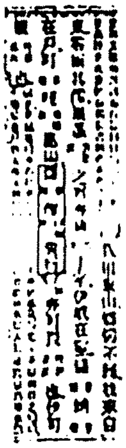
45 Hadgal,R.R., Ph.D.Thesis, Shivaji University, Kolhapur, 1982.

46 S.Bhushan and F.S.Chandra, Pramana,Vol.24, No.4, pp. 575-582 (1985)

47 N.Singh et al., Phys. Status Solidi a (Germany), Vol. 66, No.2, p-767-5 (1981).

48 Sunta, C.M., Nucl. Tracks, Vol. 10. No.1/2 pp. 47-53 1985.

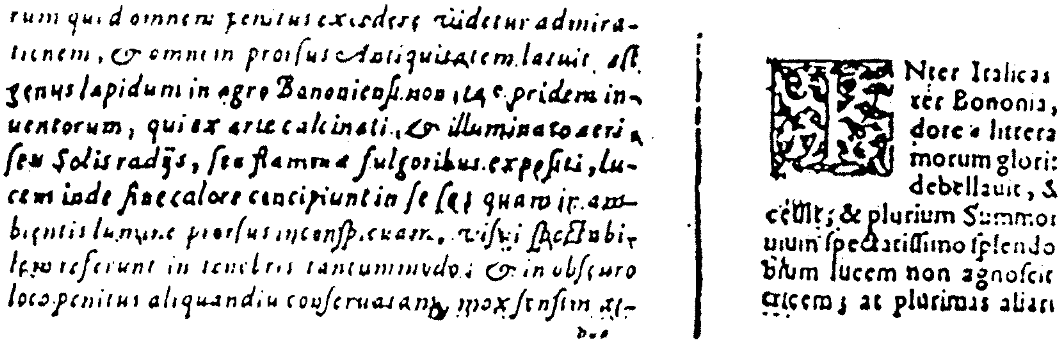
49 Dhayagude N.S., Ph.D. Thesis, Shivaji University, Kolhapur, 1984.



Reference to bioluminescence in the Chinese "Book of Odes" with commentaries

FIG. NO. 1.1

" illuminato aeri seu solis radiis, seu flammae fulgoribus expositi, lucem inde sine calore concipiunt in sase....."

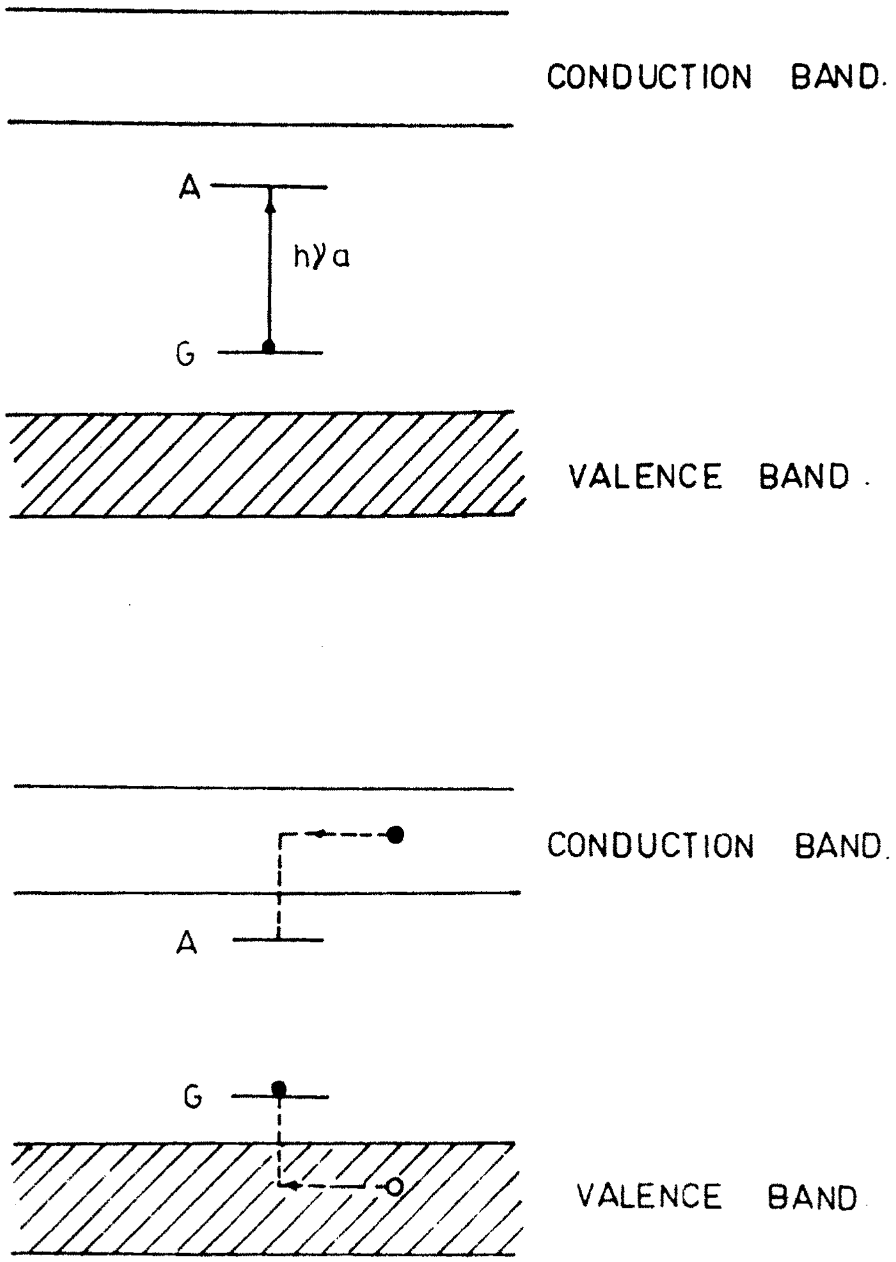


rum quid omnem penitus excedere videtur admira-
tionem, & omnem prorſus Antiquitatem latuit, eſt
genus lapidum in agro Bononienſi non ita pridem in-
uentorum, qui ex arte calcinati, & illuminato aeri,
ſeu Solis radijs, ſeu flammæ fulgoribus expoſiti, lu-
cem inde ſine calore concipiunt in ſe ſe; quam in am-
bientis lumine prorſus inconſpicuam, viſui ſtatim obi-
ter referunt in tenebris tantummodo; & in obſcuro
loco penitus aliquandiu conſeruatam, mox ſenſim at-

Nter Italicas
ter Bononia,
dore a littera
morum glori:
debellauit, S
ceſſit; & plurium Summor
uium ſpectatiſſimo ſplendo
bium lucem non agnoſcit
[illegible]; at plurimas alian

Early definition of luminescence by Licetus, as it appears in his book of 1640. Photoluminescence of the Bologna stone; when properly calcinated and illuminated either by sunlight or flames, it conceives light without heat.

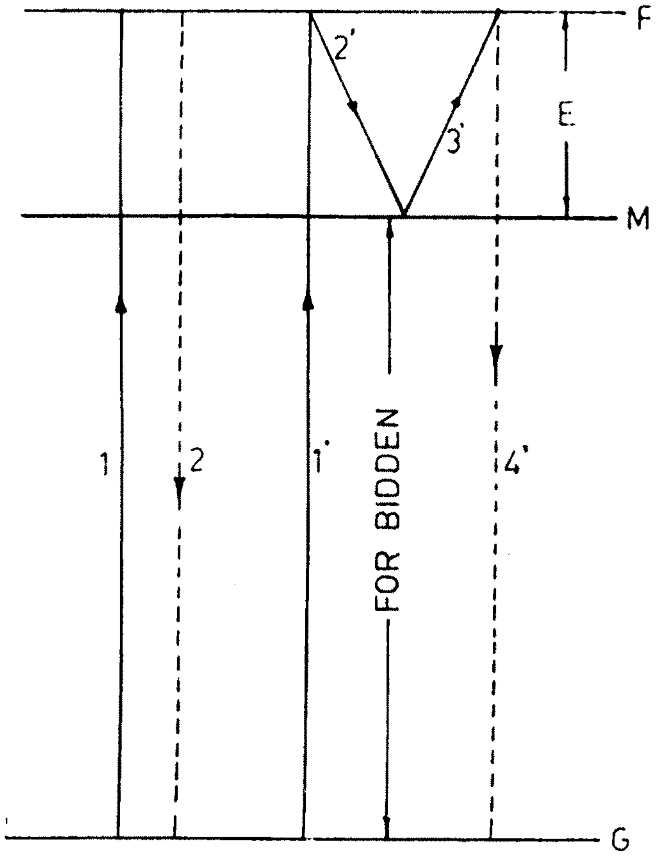
FIG. NO 1.2



THE LUMINESCENCE CENTER AND ITS EXITATION

FIG. NO 1.3

ENERGY STATES FOR FLUORESCENCE AND PHOSPHORESCENCE



G : GROUND STATE

F EXCITED STATE

M : METASTABLE STATE

E : ACTIVATION ENERGY

1 1' : EXITATION FLUORESCENCE

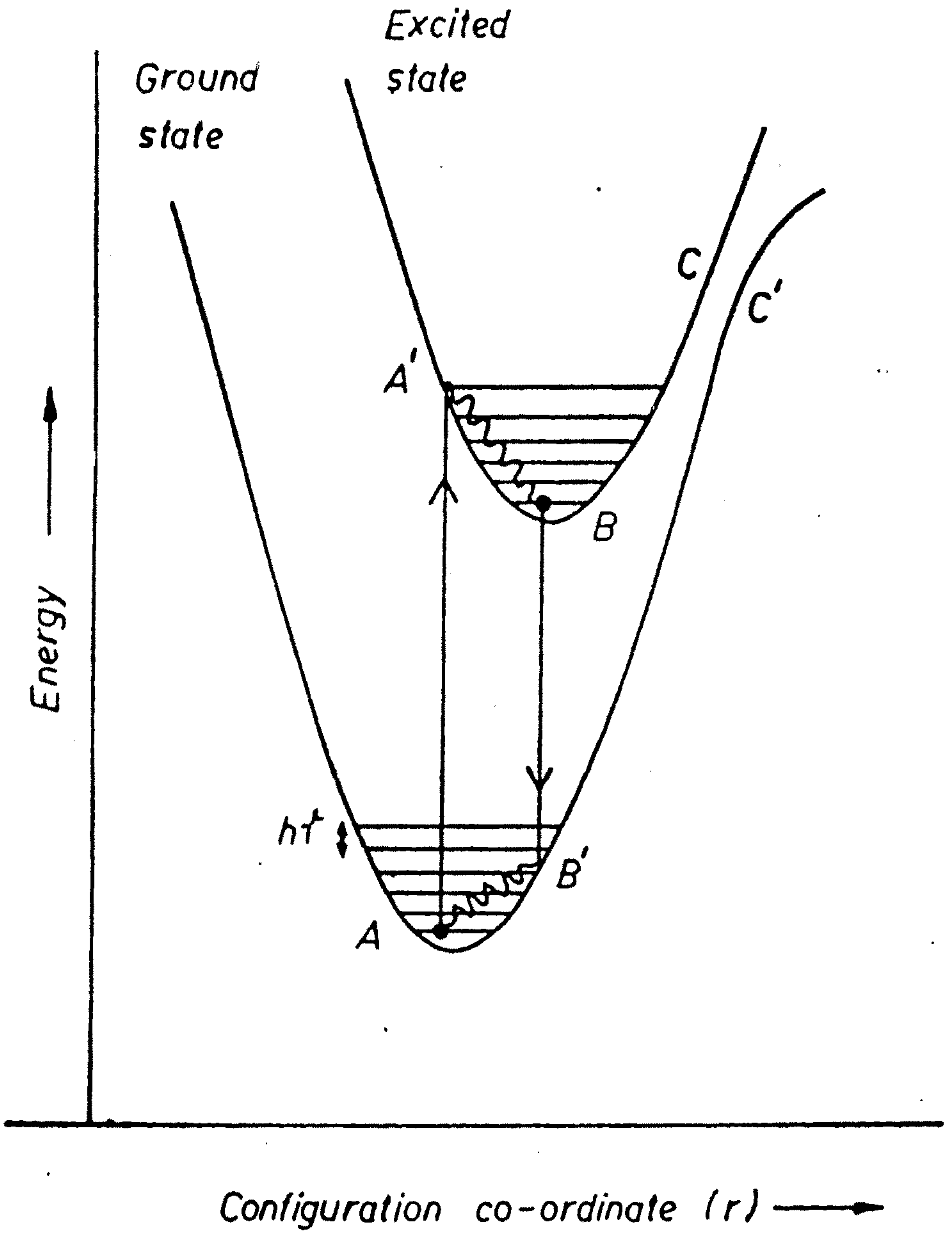
2 : FLUORESCENCE

2' : DROP IN METASTABLE LEVEL

3' : ACTIVATION THERMAL OR OPTICAL

4' : PHOSPHORESCENCE

FIG NO. 1.4



AA' : absorption transition

BB' : luminescence emission

$BCC'A$: non-radiative transition

$h\nu$: vibrational level separation

Configuration co-ordinate curve model.

FIG. NO. 1.5

ENERGY BAND MODEL

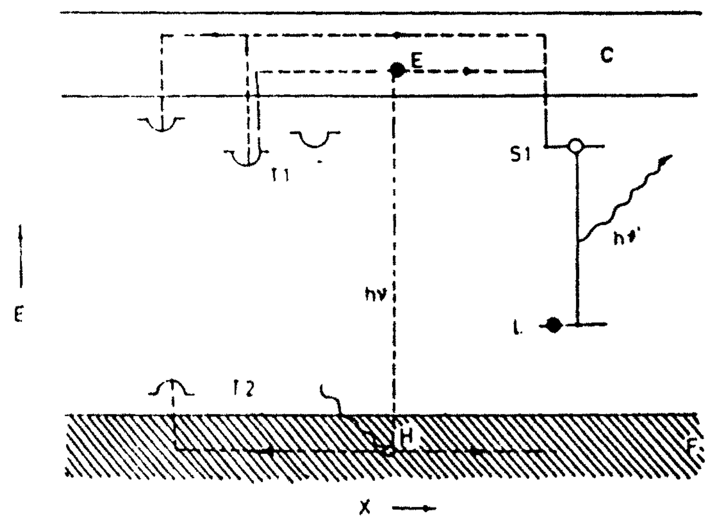


FIG. NO. 1.6

SCHON · KLASSEN'S MODEL

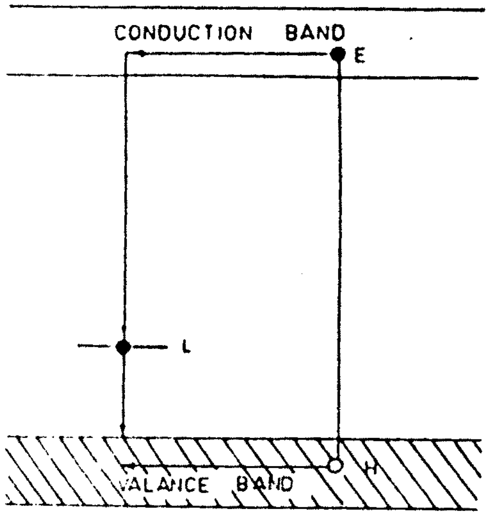


FIG. NO. 1.7

LAMBE - KLICK'S MODEL

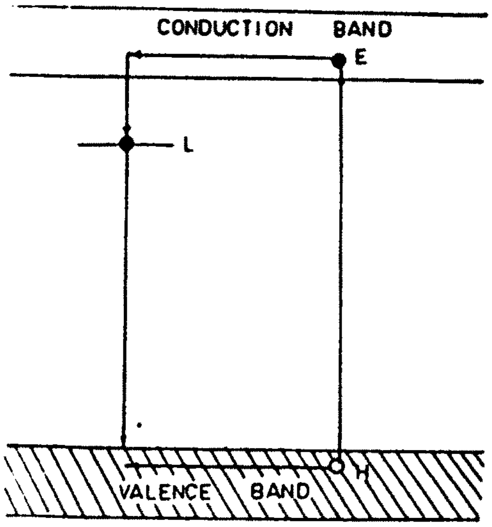


FIG. NO. 1.8

WILLIAM'S AND PRENER'S MODEL

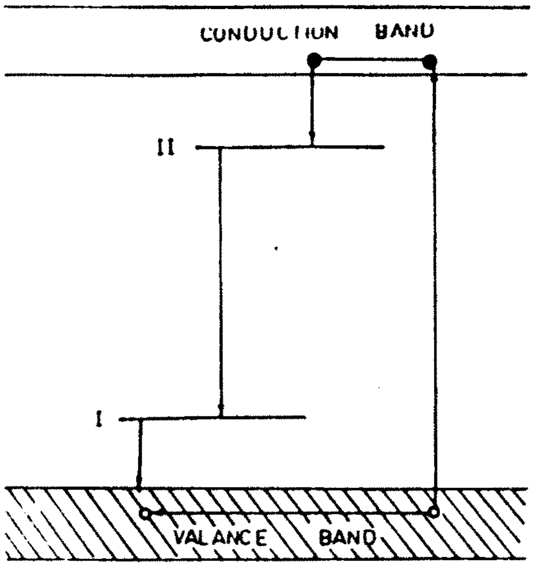


FIG. NO. 1.9

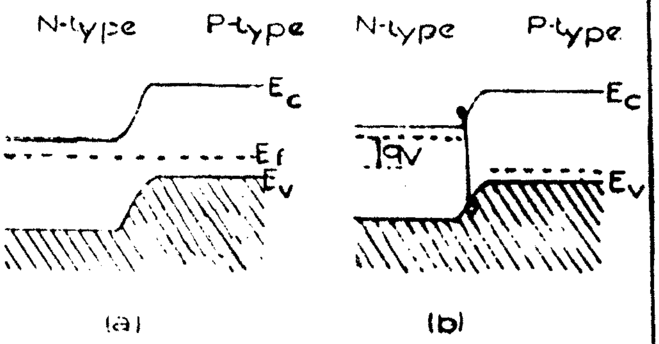


FIG. NO. 1·10

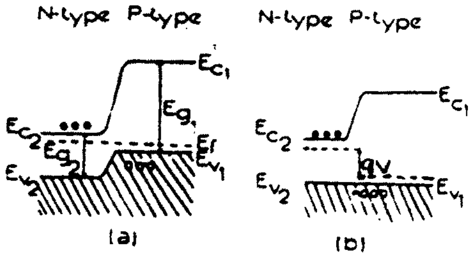


FIG. NO. 1·11

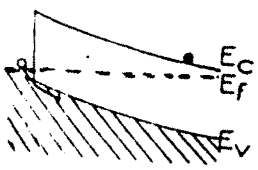
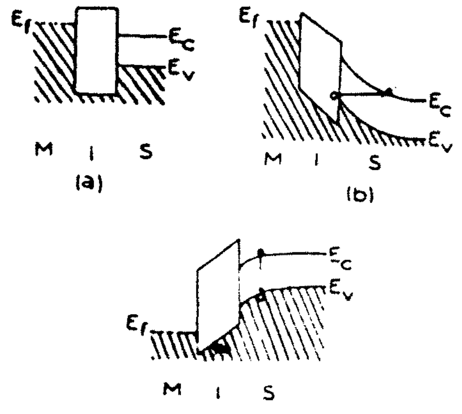


FIG. NO. 1·12



(c) FIG. NO. 1·13

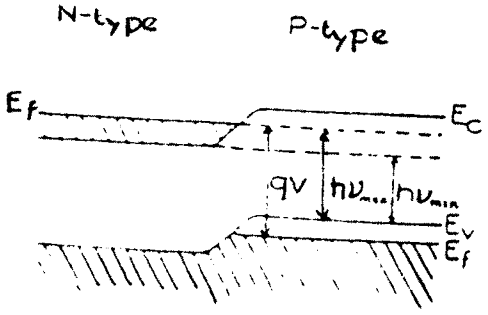


FIG. NO. 1·14

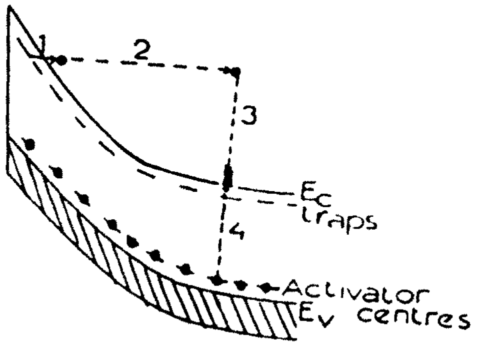


FIG. NO. 1·15